

Reactivity Control of a Dinuclear Xenophilic Species, $\text{Tp}^\# \text{Ni}-\text{RuCp}(\text{CO})_2$, via Spin Crossover across a Metal-metal Bond [$\text{Tp}^\#$: Hydrotris(4-bromo-3,5-dimethylpyrazolyl)borato]

Kazuhiro Uehara, Shiro Hikichi,^{##} and Munetaka Akita*

Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503

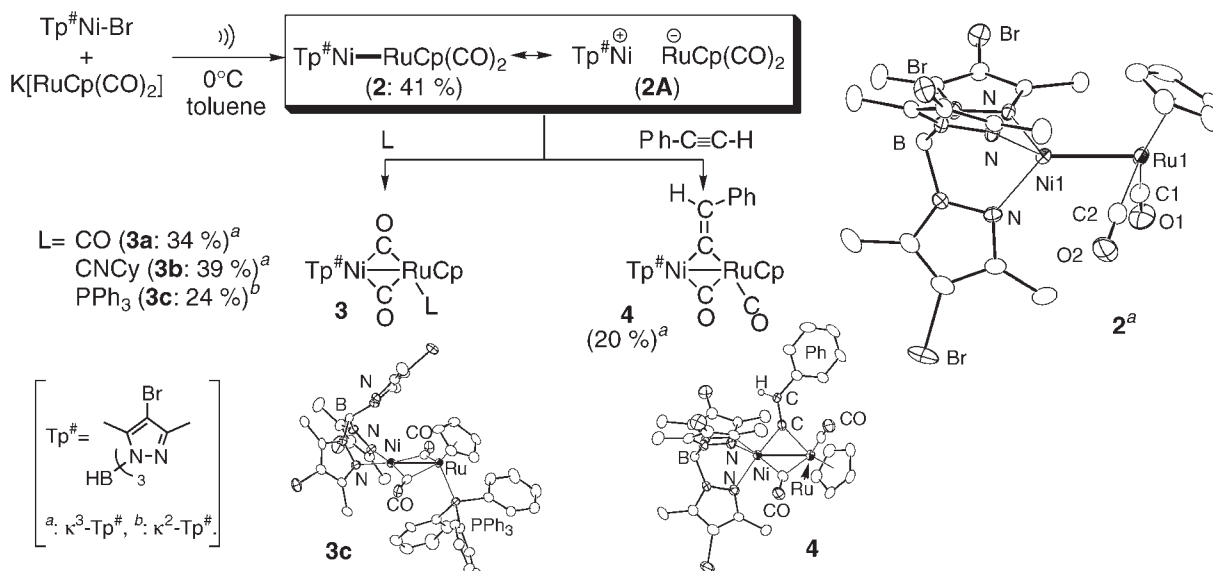
(Received August 13, 2002; CL-020690)

A high-spin, triplet xenophilic complex, $\text{Tp}^\# \text{Ni}-\text{RuCp}(\text{CO})_2$, readily reacted with 2e-donors (L) via spin crossover at Ni associated with transposition of the resultant coordinatively unsaturated site from Ni to Ru to give diamagnetic adducts, $\text{Tp}^\# \text{Ni}-\text{RuCp}(\mu\text{-CO})_2(\text{L})$.

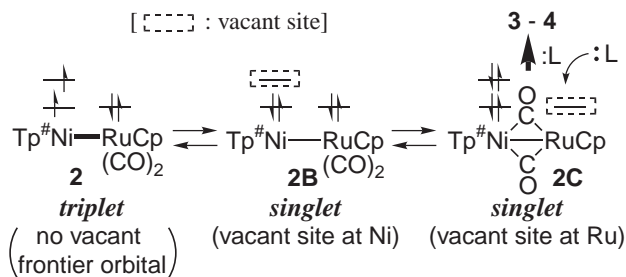
High spin organometallics are expected to display unique properties and reactivities distinct from those of closed-shell, diamagnetic organometallic species but their chemistry has not been thoroughly explored.¹ In particular, the relationship between the spin state and stability (reactivity) of electron-deficient, coordinatively unsaturated species is still in controversy. Xenophilic complexes are a polynuclear version of high spin species having a polar metal-metal bond between a coordinatively unsaturated Wernerian metal fragment and a coordinatively saturated organometallic fragment.² Previously we reported a rational synthetic method for a series of xenophilic complexes, $\text{Tp}^\text{R} \text{M}-\text{Co}(\text{CO})_4$ **1**,³ containing the $\text{Tp}^\text{R} \text{M}$ -type Wernerian metal fragment with Tp^R [hydrotris(pyrazolyl)borato]⁴ featured as a tetrahedral enforcer. Because, however, complexes **1** were too unstable to be scrutinized, reactivity of $\text{Tp}^\text{R} \text{M}-\text{M}'\text{L}_n$ -type complexes is yet to be characterized. Herein we wish to report (i) synthesis of $\text{Tp}^\# \text{Ni}-\text{RuCp}(\text{CO})_2$ **2**,⁵ the first example of a xenophilic complex containing a second row metal fragment, and (ii) a new type of reactivity of a dinuclear species emerging via spin crossover across a metal-metal bond.

The heterobimetalllic xenophilic complex **2** was prepared by

sonication of a toluene suspension of $\text{Tp}^\# \text{Ni}-\text{Br}$ and $\text{K}[\text{RuCp}(\text{CO})_2]$ (Scheme 1).⁶ The dark brown complex **2** shows chemical properties⁷ similar to those of **1**, i.e. (i) coordinatively unsaturated species with 32 valence electrons (VEs) (short of 2 VEs from a saturated structure), (ii) paramagnetic, high-spin species with a triplet ground state (μ_{eff}), (iii) connection of the two metal centers only by the metal-metal bond (no $\mu\text{-CO}$ ligand), and (iv) the polarized metal-metal bond (**2A**) [shift of the $\nu(\text{CO})$ vibrations to lower energies]. These features are also supported by X-ray crystallography.⁸ The $\text{Tp}^\# \text{Ni}$ and $\text{RuCp}(\text{CO})_2$ moieties adopt a typical tetrahedral and three-legged piano-stool structure, respectively, and the distance of the unsupported Ni-Ru bond [2.512(1) Å] is slightly shorter than those in the adducts with additional bridging ligands [2.576(1) (**3b**), 2.560(1) (**3c**), 2.579(1) Å (**4**); see below]. The CO ligands are η^1 -bonded to the Ru center with no bridging interaction with the Ni center as is evident from the linear Ru-C-O linkage [C1-O1: 175.9(8)°; C2-O2: 176.5(8)°] and the Ni...CO separations [Ni1...C1: 2.866(9) Å; Ni1...C2: 2.761(8) Å]. Despite the coordinatively unsaturated 32 VE structure, complex **2** turns out to be thermally stable, although it is sensitive to the air and moisture. The thermal stability has been ascribed to lack of a vacant frontier orbital, i.e. all frontier orbitals are occupied by electron pairs or unpaired electrons to lead to the high spin, triplet electronic configuration (see structure **2** in Scheme 2). These features are in line with the formulation as a xenophilic complex, where the tetrahedral, high spin, coordinatively unsaturated Ni fragment is bonded to the coordinatively saturated Ru center.



Scheme 1.



Scheme 2.

Despite the lack of a vacant coordination site the xenophilic complex **2** readily reacted with donors under ambient conditions to afford the coordinatively saturated adducts **3** with 34 VEs (Scheme 1). Adduct formation was also observed upon treatment with phenyl acetylene, which produced the μ -vinylidene complex **4** showing the deshielded α -carbon signal (δ_{C} 251.7). The diamagnetic products **3** and **4** were characterized by spectroscopic methods⁷ and molecular structures of **3b,c**, and **4** were confirmed by X-ray crystallography.⁸ It is notable that (i) the xenophilic complex **2** without a vacant frontier orbital reacts with donors under mild conditions, (ii) diamagnetic products **3** and **4** are obtained from the paramagnetic species **2**, (iii) donors don't add to the electron-deficient Ni center in **2** but to the Ru center, and (iv) the two CO ligands in **2** are shifted from the terminal positions to the bridging positions. The first two points suggest occurrence of spin crossover.

The results obtained can be interpreted in terms of Scheme 2.^{9,10} Judging from the structures of the adducts **3-4**, the reactive form of **2** would be a singlet species with two bridging CO ligands having a vacant site at the Ru center (**2C**). Intermediate **2C** would be formed via terminal-bridging site exchange of the CO ligands of the singlet form **2B** with the vacant site at Ni, which results from spin crossover of the original triplet form **2**. Thus the triplet species **2** reacts with electron donors through spin crossover at Ni (**2B**) followed by transposition of the resultant vacant site across the metal-metal bond, which integrates the dinuclear structure. There has been much controversy about spin crossover of organometallic species. For example, Schrock^{1c} proposed the concept of "spin-blocking", which accounted for the slow reaction of a coordinatively unsaturated high spin species toward a 2e-donor, whereas Theopold^{1d} is opposed to claiming such a tendency as a general rule. While direct evidence for **2B,C** has not been obtained, the present system can be regarded as a dinuclear version of the spin crossover system with no substantial barrier between the two spin states, as judged by the reaction features.

In conclusion, the high spin, xenophilic complex **2** is formally described not only as a resonance hybrid with the zwitterionic structure **2A** but also as an equilibrated mixture with the singlet, coordinatively unsaturated form **2C** resulting from spin crossover across the metal-metal bond, and this type of behavior is a unique feature of xenophilic species.

This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas (11228201) from the Ministry of Education, Culture, Sports, Science, and Technology, Japan.

References and Notes

Present address: Department of Applied Chemistry, School of

Engineering, University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-8656.

- a) N. Shirasawa, T. T. Nguyen, S. Hikichi, Y. Moro-oka, and M. Akita, *Organometallics*, **20**, 3582 (2001). b) S. Yoshimitsu, S. Hikichi, and M. Akita, *Organometallics*, **21**, 3762 (2002). c) R. R. Schrock, K.-Y. Shih, D. A. Dobbs, and W. M. Davis, *J. Am. Chem. Soc.*, **117**, 6609 (1995). d) J. L. Detrich, O. M. Reinaud, A. L. Rheingold, and K. H. Theopold, *J. Am. Chem. Soc.*, **117**, 11745 (1995).
- L. H. Gade, *Angew. Chem., Int. Ed.*, **39**, 2659 (2000); G. Fachinetti, G. Fochi, T. Funaioli, and P. F. Zanazzi, *Angew. Chem., Int. Ed.*, **26**, 680 (1987); G. Fachinetti, G. Fochi, T. Funaioli, and P. F. Zanazzi, *J. Chem. Soc., Chem. Commun.*, **1987**, 89; G. Kong, G. N. Harakas, and B. R. Wittlesey, *J. Am. Chem. Soc.*, **117**, 3502 (1995); G. N. Harakas and B. R. Wittlesey, *J. Am. Chem. Soc.*, **118**, 4210 (1996); See also, L. H. Gade, *Angew. Chem., Int. Ed.*, **35**, 2089 (1996).
- K. Uehara, S. Hikichi, and M. Akita, *Organometallics*, **20**, 5002 (2001).
- S. Trofimenko, "Scorpionates: The Coordination Chemistry of Polypyrazolylborate Ligands," Imperial College Press, London (1999); M. Akita and S. Hikichi, *Bull. Chem. Soc. Jpn.*, **72**, 1657 (2002).
- Tp[#]: hydrotris(4-bromo-3,5-dimethylpyrazolyl)borato.
- Sonication of a toluene suspension (10 mL) of Tp[#]Ni-Br (300 mg, 0.446 mmol) and K[RuCp(CO)₂] [prepared by reduction of Ru₂Cp₂(CO)₄ (149 mg, 0.335 mmol) with Na-K alloy in THF and dried in vacuo] gave brown precipitates, which were extracted with CH₂Cl₂ and crystallized from CH₂Cl₂-hexane. **2**: dark brown crystals (148 mg, 0.181 mmol, 41% yield). The reaction without sonication afforded a mixture of products, because the reaction was so slow as to cause concomitant decomposition of **2**.
- Selected spectroscopic data: **2**: IR (KBr) 2553 (ν_{BH}), 1953, 1891 cm⁻¹ (ν_{CO}). μ_{eff} = 2.92 μ_{B} . **3a**: 2533 (ν_{BH}), 2013, 2003, 1858, 1846, 1815, 1801, 1801 cm⁻¹ (ν_{CO}). δ_{H} (CD₂Cl₂) 5.61 (Cp), 2.35 (18H, s, Me). δ_{C} (CD₂Cl₂, -90 °C) 240.6, 199.8 (CO). **3b**: 2519 (ν_{BH}), 2173 (ν_{CN}), 1842, 1793 cm⁻¹ (ν_{CO}). δ_{H} 5.40 (5H, s, Cp), 2.33 (18H, s, Me). δ_{C} 246.5 (CO), 143.0 (CN). **3c**: 2472 (ν_{BH}), 1962, 1821, 1772 cm⁻¹ (ν_{CO}). δ_{H} 4.92 (Cp), 2.22 (9H, s, Me), 2.04 (9H, s, Me). δ_{C} 242.8 (d, J_{CP} = 12.1 Hz, CO). δ_{P} 46.5. **3d**: 2536 (ν_{BH}), 2137 (ν_{CN}), 1994, 1832, 1788 cm⁻¹ (ν_{CO}). δ_{H} 5.55 (Cp), 2.37 (6H, s, Me), 2.33 (3H, s, Me), 2.23 (6H, s, Me), 1.90 (3H, s, Me). δ_{C} 245.3 (CO), 156.9 (CN). **4**: 2524 (ν_{BH}), 2017, 1843 (ν_{CO}), 1588 cm⁻¹ ($\nu_{\text{C=C}}$). δ_{H} 5.86 (Cp), 5.32 (1H, s, =CH), 2.46, 2.41, 2.36, 2.28, 1.94, 1.73 (3H x 6, s x 6, Me). δ_{C} 251.7 (C $_{\alpha}$), 236.7, 201.2 (CO), 134.8 (=CH).
- X-ray diffraction measurements were made on a Rigaku RAXIS IV imaging plate area detector at -60 °C. Crystal data: **2**: C₂₂H₂₄N₆O₂Br₃NiRu, fw = 814.8, monoclinic, space group P2₁/n, a = 12.3721(8) Å, b = 15.2504(4) Å, c = 15.955(1) Å, β = 95.1083(7)°, V = 2998.5(3) Å³, Z = 4, d_{calcd} = 1.81 g·cm⁻³, R_1 = 0.061 (refined on F²) for 5064 data ($F > 4\sigma(F)$), wR_2 = 0.204 (all data). **3b**-(hexane)_{0.5}: C₃₂H₄₂N₇O₂BBBr₃NiRu, fw = 967.0, triclinic, space group P1̄, a = 12.5785(3) Å, b = 16.3823(5) Å, c = 11.6444(5) Å, α = 107.073(1)°, β = 109.643(2)°, γ = 68.034(5)°, V = 2056.7(1) Å³, Z = 2, d_{calcd} = 1.56 g·cm⁻³, R_1 = 0.058 for 6832 data ($F > 4\sigma(F)$), wR_2 = 0.188 (all data). **3c**-CH₂Cl₂: C₄₁H₄₁N₆O₂BBPBr₃NiRu, fw = 1162.0, triclinic, space group P1̄, a = 12.628(1) Å, b = 15.784(3) Å, c = 12.553(1) Å, α = 91.157(7)°, β = 114.240(8)°, γ = 83.816(6)°, V = 2267.5(6) Å³, Z = 2, d_{calcd} = 1.70 g·cm⁻³, R_1 = 0.075 for 6008 data ($F > 4\sigma(F)$), wR_2 = 0.201 (all data). **4**: C₃₆H₄₄N₆O₂BBBr₃NiRu, fw = 1003.1, triclinic, space group P1̄, a = 12.044(2) Å, b = 16.873(3) Å, c = 11.170(2) Å, α = 96.099(6)°, β = 113.258(5)°, γ = 104.55(1)°, V = 1963.8(6) Å³, Z = 2, d_{calcd} = 1.70 g·cm⁻³, R_1 = 0.068 for 5316 data ($F > 4\sigma(F)$), wR_2 = 0.190 (all data).
- Complex **4** should be formed via coordination of Ph-C≡C-H at Ru in **2C**, 1,2-H-shift giving a η^1 -vinylidene ligand and site exchange with the μ -CO ligand. M. I. Bruce, *Chem. Rev.*, **98**, 2797 (1998).
- Analogous addition reactions were also observed for **1** (M=Ni, Tp^R=Tp[#]) and, therefore, these types of properties can be regarded as unique properties of xenophilic complexes containing a Tp^RM fragment. K. Uehara, S. Hikichi, and M. Akita, unpublished results.